PIGMENT HANDBOOK

Volume I

PROPERTIES AND ECONOMICS

Second Edition

Edited by
PETER A. LEWIS

EPO - DG 1
07. 04. 2010
118

A Wiley-Interscience Publication
JOHN WILEY & SONS

New York • Chichester • Brisbane • Toronto • Singapore

The tables and data contained in this book are provided for informational and educational purposes only. While they are based on experience and information believed to be reliable, the authors and the publisher make no guarantee of their accuracy or completeness and assume no liability in connection therewith.

Library of Congress Cataloging in Publication Data:

Pigment handbook.

"A Wiley-Interscience publication."
1. Pigments. I. Lewis, Peter; 1946– .
TP936.P58 1987 667'.29 87-13358
ISBN 0-471-82833-5 (v. 1)

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Pr

This
book,
work
ton. I
rathe
exper
pigme
obtai
the pl
the w
sentia
extra
major
ments
By
merel
vious
date f
volum
chapt
pigme
stage

Cuprous Oxide

I-J-a

WALTER O. BAYER
Consultant
Phoenix, Maryland

RONALD J. DIETRICH
Product Manager
SCM Metal Products
Cleveland, Ohio

ERHARD KLAR
Manager, Particle Technology
SCM Metal Products
Cleveland, Ohio

Red Copper Oxide
Colour Index Number 77402
Chemical Formula Cu_2O (MW 143.1)
Chemical Composition (wt %)

Cu	88.82
O	11.18
	100.00

TYPICAL PROPERTIES

	Cuprous Oxide	
	Red	Purple
Appearance	Red powder	Purple powder
Density		
Solid (g/cm^3)	6.0	6.0
(lb/gal)	50.0	50.0
Bulk (g/cm^3)	1.7	2.3
Refractive index	2.705	2.705
Tinting strength	High	Low
Oil absorption (lb/100 lb)	6.0–9.0	6.0–9.0
Particle size SSD (μm)	2.0–4.0	10–16

ECONOMICS

The price of cuprous oxide varies with that of copper metal; the average annual prices in the United States for the period 1977–1983 are shown in Table 1. These prices are calculated from data obtained through the U.S. Department of Commerce.[1] Also shown in Table 1 are the corresponding shipments of cuprous oxide during this period. The majority of cuprous oxide shipments reported to the U.S. Department of Commerce by domestic manufacturers is believed to be consumed in the manufacture of antifouling paints for government, commercial, and pleasurecraft ship bottoms. The report does not differentiate between government and private consumption nor does it distinguish between pigment and nonpigment applications.

Table 1 Cuprous Oxide Shipments and Pricing[1]

Year	Tons Shipped	Average Anoual Price ($/lb)
1977	3459	0.84
1978	3532	0.98
1979	4166	1.14
1980	4786	1.21
1981	5135	1.04
1982	4883	1.12
1983	4993	1.23

HISTORICAL BACKGROUND[2,3]

The treatment of ship bottoms to prevent fouling by marine life has been traced to the 5th century B.C., but the use of copper as an antifoulant does not appear to have been suggested until 1825 when a patent was granted for a composition that probably contained copper. Much has been said about copper sheathing of ship bottoms of ancient times, but the first authenticated use of copper sheathing on wooden ship bottoms was on *H.M.S. Alarm* in 1758. The first American naval ship to be copper sheathed was the frigate *Alliance* in 1781.

Copper provided a good antifouling surface, but it could no longer be used when wood was replaced by steel for ship bottoms because of the corrosion of steel produced by the galvanic action between copper and iron in seawater. This is where cuprous oxide found its niche in history. It can be used in paint for ship bottoms to prevent fouling by marine life without causing harmful corrosion of steel by galvanic action.

Because of the poor and variable performance of early antifouling paints and because of their high military importance, the navy decided around 1909 to develop and produce its own antifouling paints. This led to the development of many successful antifouling paint formulations (see Table 2).

Table 2 Representative Antifouling Paint Formulations Calling for Specification Cuprous Oxide as Pigment (see Table 3)

Paint Formulation	Formula Number
MIL-P-15931B	
Paint, Antifouling, Vioyl, Red	121/63
MIL-P-16189B	
Paint, Antifouling, Vinyl, Black	129/63
MIL-P-19449B	
Paint, Antifouling, Cold Plastic, Black	146/50
MIL-P-19451B	
Paint, Antifouling, Cold Plastic, Ship Bottom	Navy 105
HIL-P-19452A	
Paint, Antifouling, Hot Plastic, Ship Bottom	Navy 15 HPN
MIL-P-22299A	
Paint, Antifouling, Polyisobutylene	134
CGS-529-3	
U.S. Coast Guard, Vinyl, Red	NDRC-AF-14
CGS-52-3C	
U.S. Coast Guard, Vinyl, Red	—
CGS-52P-6	
U.S. Coast Guard, Vinyl, Red	NDRC-AF-14
FS-11-63	
U.S. Coast Guard Purchase Description, Vinyl, Red	—
TT-P-117A	
Paint, Antifouling, Bottom	—

MAJOR REASONS FOR USE[3–6]

Cuprous oxide is one of the oldest and one of the most effective antifoulants. Fouling of ship bottoms by marine life results in loss of ship speed, overconsumption of fuel, corrosion, and more frequent drydocking (to remove the fouling growth). Saroyan[3] credits the development and use of effective antifouling paints (that permitted U.S. naval vessels to stay out of drydock for 18 months rather than the usual 9 months) as instrumental in substantially shortening the war with Japan.

Fouling consists of a variety of organisms which attach themselves to objects immersed in seawater or freshwater including such things as barnacles, worms, algae, moss, or seaweed. The latter three are referred to as *grass* in marine circles. These vary in species and in intensity of growth with water temperature, degree and composition of the salts dissolved in the water, light intensity, and water currents. A good reference for greater detail on fouling is *Marine Fouling and Its Prevention*, prepared for the Bureau of Ships, Navy Department, by Woods Hole Oceanographic Institution in Woods Hole, Massachusetts. It is obtainable from the U.S. Naval Institute of Annapolis, Maryland, and printed by George Banta Co., Inc., Menasha, Wisconsin.

With these great variations possible in the type and amount of fouling, it is understandable that no one antifouling material is ideal against all types of fouling, particularly if the vessel, in its travels, will be exposed to varying conditions. Many of the better grades of commercial antifouling paints offered today for ships that travel to various parts of the world will often have a combination of two or more antifoulants for maximum effectiveness against the variety of fouling organisms they will encounter.

Vessels whose travel is limited may often obtain satisfactory results with smaller quantities of a single antifoulant. This is particularly true if they are confined to freshwater. Cuprous oxide is frequently used in conjunction with tributyltin compounds, such as tributyltin oxide (TBTO) or tributyltin fluoride (TBTF), in the antifouling paints used on commercial vessels engaged in far-reaching or worldwide travel today. Mercury, arsenic, and organolead compounds have also been used as antifoulants in paint in the past but find little use today, since mercury and arsenic compounds in antifouling paints are not permitted by the governments of most of the major countries; and organolead antifoulants, although permitted by Great Britain and some other countries, are not viewed favorably by the Environmental Protection Agency of the United States.

The quantity of cuprous oxide may vary from 20 to 80% by weight in antifouling paints where it is the only toxicant. It has been determined[5] that a paint will provide effective antifouling protection under average conditions if a minimum of 1 mg Cu/100 cm^2 (of paint surface) goes into solution in 24 h. The rate of solution can vary in a specific formula with the temperature, flow, and salinity of the water. An antifouling paint using cuprous oxide must have its binder composition adjusted for water resistance to enable the copper to solubilize at a sufficient rate to prevent fouling but not at a materially faster rate which would deplete the copper content of the film too rapidly and reduce the effective life of the coating.

In certain formulations, where color is important (black antifouling paints for submarines[3]), cuprous oxide must give way to alternate antifouling agents or be used with them. In recent years, lower tinting strength grades of purple cuprous oxide have found increased usage in a variety of colors where the color of the cuprous oxide can be masked by other pigments. White, very clean pastel shades, and some bright clean solid colors cannot be made using high percentages of cuprous oxide and rely on tributyltin compounds for the antifoulant. Special dispersion techniques have increased the variety of colors that can be

obtained when using cuprous oxide in lighter or cleaner shades.

Presently available antifouling coatings that contain cuprous oxide have protected ship bottoms effectively for periods of up to 3 years. Specially formulated coatings using cuprous oxide with tributyltin compounds and applied in multiple coats are so designed that the toxicant-depleted surface layer of antifouling paint becomes mechanically weaker than the undepleted underfilm and also changes color. This depleted layer can be scrubbed off by a diver or by a radio-controlled device on a mechanism referred to as a SCAMP without the vessel going into drydock. This exposes undepleted antifouling coating which has the same color as when the coating was originally applied and enables the ship to operate for another lengthy period without drydocking. This procedure has a large cost advantage over periodic drydocking and does not take the ship out of service since it can be accomplished dockside while the vessel is loading or unloading. Vessels using this system have gone as long as 5 years between drydockings.

Other uses for cuprous oxide are as a fungicide in horticulture control preparations and as a colorant in ceramic glazes and glasses.

PIGMENT MANUFACTURE

Commercial processes used in the manufacture of cuprous oxide include electrolysis, oxidation and grinding of metallic copper particles, partial oxidation and grinding of copper precipitates, grinding of copper scale, and various chemical processes that are proprietary.

The electrolytic process[7,8] is predominantly used by foreign producers for the production of high-purity fine cuprous oxide. The process involves electrolysis of a solution of sodium chloride (containing a small amount of caustic soda) between copper electrodes in a diaphragm cell. Since no refinement takes place, it is essential to use pure copper anodes. The cell temperature is kept below 90°C to minimize the generation of cupric oxide. The fineness of the cuprous oxide can be controlled through variation of the current density and salt concentration. Particle size decreases with increasing current density and increasing salt concentration. A typical current density is 40 A/ft^2. The cuprous oxide sludge is filtered, washed, and dried at low temperature. The finer the particle size becomes, the more the red color improves. Still finer particle size, obtainable also through the addition of lyophilic protein colloids such as glue, renders the cuprous oxide yellow. Electrolytically produced cuprous oxide tends to be unstable as deposited but may be stabilized by various treatments (e.g., fatty acids, dextrin).

Several major U.S. manufacturers use controlled processes that involve the oxidation of finely divided metallic copper at 1700–1900°F, grinding, and classifying. These products are of high quality, stable against oxidation, and meet the military specifications required for today's antifouling pigment grades.

PIGMENT GRADES

The grades of cuprous oxide used within the paint industry have essentially been reduced to three major types.* These pigments are of equal quality and meet the requirements of MIL-P-15169B covering the procurement of cuprous oxide for antifouling paints. The major differences between these pigments relate to particle size distributions which are a result of the techniques used to manufacture the pigment. These differences can be noticed visually by the

* The lower-quality pigment grades discussed in the previous edition of this handbook are no longer used as pigment grades, because both paint manufacturers and users have standardized on the higher-quality pigments which have proved their superior consistency over the last 20 years over the slightly less expensive pigment grades that were made primarily from industrial by-products.

color of the cuprous oxide pigment. Each grade has its own advantages. The red cuprous oxide has been referred to as *High Tint* and is preferred by some paint manufacturers who manufacture red antifouling paints. The purple pigment is referred to as *Low Tint* and is widely used in all applications because its low tint strength allows the paint manufacturer to produce a wider range of colored antifouling paints, especially blues, blacks, and greens, for government, commercial, and pleasurecraft paint markets. The third grade has been referred to as *Lo Lo Tint* and allows the paint manufacturer to produce higher-clarity colored antifouling paints for special applications.

Cumulative particle size distribution curves for red and purple grades are given in Fig. 1 and reveal the much finer particle size of the red pigment.

The spectral reflectance curves given in Fig. 2 for the red and purple grades of cuprous oxide clearly show the differences in the reflectance of light from these two pigments. Figure 3 is a photomicrograph of commercial Grade Red (high tint) cuprous oxide.

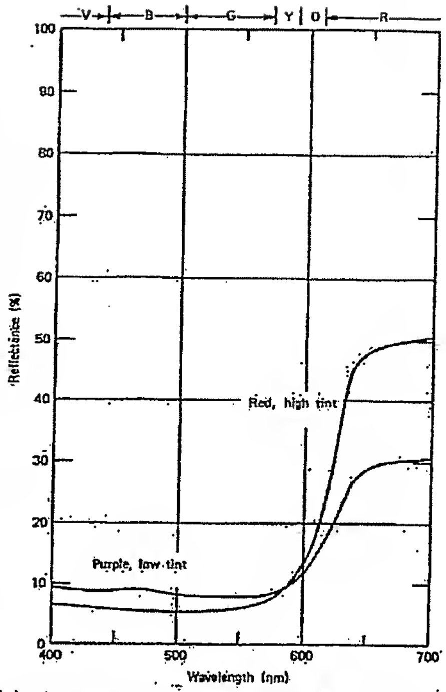

Fig. 2. Spectral reflectance curves for commercial purple (low tint) and red (high tint) cuprous oxide.

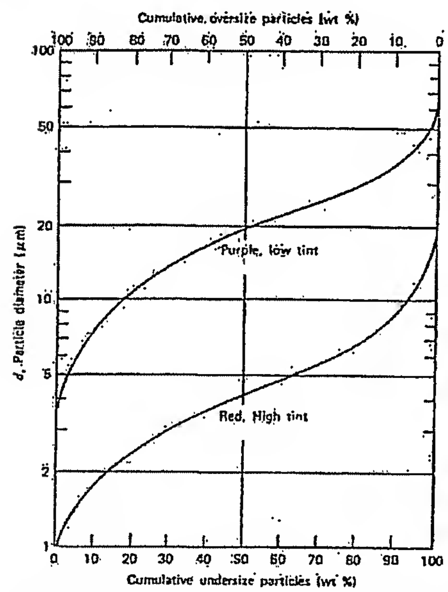

Fig. 1. Cumulative particle size distribution curves for commercial grades of purple (low tint) and red (high tint) cuprous oxide (Coulter counter).

Fig. 3. Electron photomicrograph of red (high tint) cuprous oxide.

Table 3 Property Specifications for Cuprous Oxide Used in Antifouling Paints (Incomplete)

	Military MIL-P 15169B	ASTM D912-65
Cuprous oxide (Cu_2O), minimum (%)	95.0	97.0
Cuprous oxide + free copper, minimum (%)	97.0	NS[a]
Total copper, minimum (%)	86.0	86.0
Total reducing power as Cu_2O, minimum (%)	97.0	97.0
Metals other than copper maximum (%)	0.50	0.5
Cupric oxide (CuO), maximum (%)	NS[a]	NS[a]
Combined chlorides as Cl and sulfates as SO_4, maximum (%)	0.50	0.50
Acetone-soluble matter, maximum (%)	0.50	0.50
Water, maximum (%)	0.50	NS[a]
Residue, total, 325 mesh sieve, maximum (%)	0.5	0.5
Stability: loss of total reducing power, maximum (%)	2.0	2.0

[a] NS = not specified.

PIGMENT SPECIFICATIONS AND MANUFACTURERS

Table 3 lists the major properties demanded of a cuprous oxide that is used in antifouling paints as specified by two standard specifications. The two U.S. manufacturers presently producing cuprous oxide to meet these two specifications are given in Table 4.

Table 4 Manufacturers of Antifouling Cuprous Oxide Pigment Meeting Standard Specifications[a]

Manufacturer Coding and Trade Names	Military MIL-P 15169B[b]	ASTM D912-65[b,c]
ACM		
Red Copp (High Tint)	M	M
Purple Copp (Low Tint)	M	M
Purple Copp (Lo Lo Tint)	M	M
SCM		
AA Purple (Low Tint)	M	M

[a] See Table 3 for specification details.

[b] M = meets specifications.

[c] Meets specification except for 97.0% minimum cuprous oxide.

REFERENCES

1. U.S. Department of Commerce, Bureau of the Census, Current Industrial Reports, Inorganic Chemicals and Gases, 1977–1983.
2. Miller, S., NPVLA Marine Coatings Conference, New York, May 4, 1967.
3. Saroyan, J. R., NPVLA 80th Annual Meeting, San Francisco, November 1, 1967.
4. Saroyan, J. R., "Marine Biology in Antifouling Paints," *J. Paint Technol.*, 41(531), 285 (Apr. 1969).
5. Saroyan, J. R., Lindner, E., Dooley, C. A., and Bleile, H. R., "Barnacle Cement—Key to Second Generation Antifouling Coatings," *Ind. Eng. Chem. Prod. Res. Dev.*, 9(2), 122 (June 1970).
6. Nowacki, L. J., "Ship Bottom Coatings," NPVLA Marine Coatings Conference, New York, May 4, 1967.
7. Arend, A. G., "The Manufacture of Cuprous Oxide," *J. Paint Technol.*, 13(151), (July 1948).
8. Hurd, L. D., U.S. Patent 2,273,643, "Electrolytic Preparation of Yellow Cuprous Oxide" (Feb. 17, 1942).